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[Material] Abstract 1

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[Name of the Document] Claim(s)

[Claim 1] A stacked photovoltaic element  
5 comprising a plurality of unit photovoltaic elements  
each composed of a pn- or pin-junction, connected to  
each other in series, characterized in that a zinc  
oxide layer is provided at least one position between  
the unit photovoltaic elements, and the zinc oxide  
10 layer has resistivity varying in a thickness direction  
thereof.

[Claim 2] The stacked photovoltaic element  
according to Claim 1, characterized in that zinc oxide  
of the zinc oxide layer on a side of being in contact  
15 with a p-layer has a higher resistivity than that on a  
side of being in contact with an n-layer.

[Claim 3] The stacked photovoltaic element  
according to Claim 2, characterized in that a  
resistivity of the zinc oxide continuously decreases in  
20 the zinc oxide layer from a side of the zinc oxide  
layer in contact with the p-layer towards a side of the  
zinc oxide layer in contact with the n-layer.

[Claim 4] The stacked photovoltaic element  
according to any one of Claims 1 to 3, characterized in  
25 that a resistivity of zinc oxide of the zinc oxide layer  
is  $2 \times 10^0 \Omega\text{cm}$  or more and  $5 \times 10^3 \Omega\text{cm}$  or less.

[Claim 5] The stacked photovoltaic element

according to any one of Claims 1 to 4, characterized in that a high resistant portion of zinc oxide of the zinc oxide layer has  $5 \times 10^2 \Omega\text{cm}$  or more and  $5 \times 10^3 \Omega\text{cm}$  or less.

5           [Claim 6] The stacked photovoltaic element according to any one of Claims 1 to 5, characterized in that at least one of the plurality of the unit photovoltaic elements has a pin-junction comprising an i-type layer composed of amorphous Si:H.

10           [Claim 7] The stacked photovoltaic element according to any one of Claims 1 to 5, characterized in that at least one of the plurality of the unit photovoltaic elements has a pin-junction comprising an i-type layer composed of microcrystalline Si.

15           [Claim 8] The stacked photovoltaic element according to any one of Claims 1 to 5, characterized in that at least one of the plurality of the unit photovoltaic elements has a pin-junction comprising an i-type layer composed of single-crystalline or poly-  
20 crystalline Si.

            [Claim 9] A method for producing a stacked photovoltaic element comprising an intermediate layer between photovoltaic elements each having a pn- or pin-junction,

25           characterized in that a first layer mainly composed of indium oxide is stacked on at least one interface with the photovoltaic element and then a

second layer mainly composed of zinc oxide is stacked on the first layer to form the intermediate layer.

[Claim 10] The method according to Claim 9 for producing a stacked photovoltaic element, characterized  
5 in that the second layer is formed to be thicker than the first layer.

[Claim 11] The method according to Claim 9 or 10 for producing a stacked photovoltaic element, characterized in that the first layer is formed to have  
10 a thickness of 1 nm or more and 50 nm or less.

[Claim 12] The method according to any one of Claims 9 to 11 for producing a stacked photovoltaic element, characterized in that the second layer is formed at a rate higher than that of the first layer.

15 [Claim 13] The method according to any one of Claims 9 to 12 for producing a stacked photovoltaic element, characterized in that the second layer is formed at a temperature lower than that of the first layer.

20 [Claim 14] A stacked photovoltaic element comprising an intermediate layer between photovoltaic elements each having a pn- or pin-junction, characterized in that the intermediate layer comprises a first layer and a second layer stacked in this order  
25 on at least one interface with a photovoltaic element, the first layer being mainly composed of indium oxide and the second layer being mainly composed of zinc



oxide.

[Claim 15] The stacked photovoltaic element according to Claim 14, characterized in that the second layer is thicker than the first layer.

5 [Claim 16] The stacked photovoltaic element according to Claim 14 or 15, characterized in that the first layer has a thickness of 1 nm or more and 50 nm or less.

[Claim 17] The stacked photovoltaic element  
10 according to any one of Claims 14 to 16, characterized in that the second layer has a higher transmittance than the first layer at a wavelength of 800 nm.

[Name of the Document] Specification

[Title of the Invention] Stacked Photovoltaic Element  
and Method for Producing the Same

[Field of Art]

5 [0001]

The present invention relates to a stacked photovoltaic element comprising at least two power-generating function units, and a method for producing the same.

10 [Background Art]

[0002]

A photovoltaic element is a device which converts incident light energy into electric energy. A solar cell is a photovoltaic element which converts solar rays as white light into electric energy. It is characterized by efficiently converting light over a wide wavelength range into electric energy. It is necessary to efficiently absorb light over a wide wavelength range in order to achieve a high conversion efficiency.

20

[0003]

A stacked photovoltaic element, which is formed by stacking a plurality of photovoltaic elements each containing a photoactive layer having a different band gap from each other is known as one of the solutions to achieve a high conversion efficiency. This stacked photovoltaic element has one photovoltaic element

25

having a photoactive layer of larger band gap on a  
light incident side or thinner photoactive layer, and  
another photovoltaic element having a semiconductor of  
smaller band gap or thicker photoactive layer in this  
5 order from the light incident side, the former  
absorbing light of shorter wavelengths and the latter  
absorbing light of longer wavelengths which the former  
transmits. The stacked photovoltaic element,  
therefore, can more efficiently absorb and utilize  
10 light over a wider wavelength range.

[0004]

It is essential to provide each photovoltaic  
element having a photoactive layer having a different  
band gap with light of a wavelength in a range suitable  
15 for that element, because a wavelength range of  
incident light which each photovoltaic element can  
utilize varies depending on the band gap of a  
semiconductor used as the photoactive layer for that  
element. In other words, photon cannot be absorbed by  
20 the semiconductor when photon has lower energy than the  
band gap of the semiconductor. In such a case, it only  
passes through the semiconductor without being  
utilized. On the other hand, photon having higher  
energy than the band gap of the semiconductor cannot be  
25 fully utilized although it can be absorbed, because  
potential energy of electron which can be produced when  
the electron is excited is limited by magnitude of the

band gap, whereby the difference between the band gap energy and photon energy cannot be utilized. It is therefore essential to design a stacked photovoltaic element to selectively introduce light of shorter  
5 wavelength range into a photovoltaic element on the incident light side and light of longer wavelength range into another photovoltaic element arranged under the above element.

[0005]

10           One of the known solutions is to provide an intermediate layer as a light-reflecting layer between these photovoltaic elements. For example, Patent Document 1 or Non-patent Document 1 disclose a method for providing an electroconductive intermediate layer  
15 each between the elements which reflects light of shorter wavelength and transmit light of longer wavelength. Patent Document 2 discloses a method for adjusting the thickness of a selective reflection layer in such a way to increase electric current flowing  
20 through a photovoltaic element on the incident light side by setting its peak reflectivity to the maximum wavelength of spectral sensitivity of the photovoltaic element on the incident light side. Patent Document 3 discloses a method for enhancing efficiency of a  
25 stacked photovoltaic element by a selective reflection layer of stacked structure having a higher reflectivity for the shorter wavelength range which the upper

photoelectron conversion layer can absorb more easily,  
and a lower reflectivity for the longer wavelength  
range which the lower photoelectron conversion layer  
can absorb more easily for transmission. Each of these  
5 techniques uses a dielectric layer of  $\text{SnO}_2$ ,  $\text{ZnO}$ , ITO or  
the like as the selective reflection layer, to prevent  
light of short wavelength, which should be absorbed by  
the photovoltaic element on the incident light side,  
from being absorbed by the lower photovoltaic element  
10 and thereby to enhance conversion efficiency of the  
photovoltaic element on the incident light side.

[0006]

[Patent Document 1]

Japanese Patent Application Laid-Open No. S63-  
15 77167

[Patent Document 2]

Japanese Patent Application Laid-Open No. H2-  
237172

[Patent Document 3]

20 Japanese Patent Application Laid-Open No. 2001-  
308354

[Non-patent Document 1]

Kenji Yamamoto, "Thin-film polycrystalline silicon  
solar cell", Applied Physics, The Japan Society of  
25 Applied Physics, May, 2002, Vol.71, No.5, p.524 to 527

[Disclosure of the Invention]

[Problem to be Solved by the Invention]

[0007]

As discussed above, the extensive studies on intermediate layers have produced the intermediate layers good to some extent. However, there are  
5 problems to be solved to satisfy the demands for improved optical and electrical characteristics, compatibility with a semiconductor layer, and deposition rate.

[0008]

10 For example, the following problems occur when the above-described electroconductive reflection layer is provided as the intermediate layer.

[0009]

A photovoltaic element of large area, comprising  
15 unit elements stacked on each other in series, e.g., as shown in Fig. 1, has electrical defects within the element, resulting from dust generated during the deposition step, or irregularities or foreign matter on the surface of a substrate. In Fig. 1, numeral 100  
20 denotes the stacked photovoltaic element; 101: substrate, 102: second photovoltaic element, 103: zinc oxide layer, 104: first photovoltaic element, 105: electroconductive layer as transparent electrode, 106: short circuit in the second photovoltaic element, and  
25 107: short circuit in the first photovoltaic element. The electrical defects inevitably associated with the large area deteriorate the element characteristics

resulting from decreased shunt resistance and fill factor (FF). One of the effective means to solve these problems is a method (passivation) in which a photovoltaic element is normally dipped in an electrolytic solution and an electric current is passed through it to selectively remove a part of an electroconductive layer outside of an electric defect. However, for a stacked photovoltaic element comprising a lower photovoltaic element layer, an intermediate layer, an upper photovoltaic element layer and an electroconductive layer on a substrate, the above procedure can partly remove the electroconductive layer on the first photovoltaic element layer as the upper layer containing the defect, but cannot remove the intermediate layer on the second photovoltaic element layer as the lower layer containing the defect. As a result, short-circuit current flows through the defect in the lower layer to decrease electromotive force of the lower photovoltaic element. Short-circuit current cannot be effectively prevented from spreading into the intermediate layer for various reasons. In particular the intermediate layer should have a certain thickness to function as the reflection layer, and should satisfy the other considerations, e.g., compatibility with the semiconductor layers with which it is in contact on both sides and series resistance. These requirements

limit a range in which the resistivity of the materials  
can be adjusted. Moreover, additional junctions  
generated between the photovoltaic elements and an  
intermediate layer of a different material therebetween  
5 inevitably deteriorate characteristics which are  
accompanied by decreased FF. Still more, a plurality  
of layers inserted to prevent a reduced shunt  
resistance further increase junction number, thus  
further aggravating the interfacial problems.

10 [0010]

As discussed above, incorporation of an  
intermediate layer as a selective reflection layer for  
increasing photocurrent involves the adverse effect of  
decreased electromotive force of the photovoltaic  
15 element.

[0011]

Moreover, the method disclosed by Patent Document  
3, although giving a selective reflection layer  
structure satisfying the light reflection and light  
20 transmission characteristics, is found to be still  
insufficient in producing the intermediate layer having  
no adverse effect on the photovoltaic element and  
having good connection with the photovoltaic element.  
For the intermediate layer to have sufficient  
25 characteristics, the following technical requirements  
should be satisfied.

[0012]



The intermediate layer should be kept in good ohmic contact with the semiconductor layer under the intermediate layer. It should be formed in such a way to cause little damages to the underlaying  
5 semiconductor layer by chemical modification (e.g., by oxidation) or physical modification (e.g., by ion-caused damages). Moreover, it should have an adequate resistivity and film thickness, and should be designed to control lateral flow of shunt current via the  
10 intermediate layer.

[0013]

It is an object of the present invention to provide a stacked photovoltaic element exhibiting a high conversion efficiency realized by producing large  
15 photocurrent without causing decreased electromotive force in consideration of the above problems.

[0014]

It is another object of the present invention to provide a stacked photovoltaic element of high  
20 conversion efficiency, capable of efficiently collecting energy over an entire wavelength range of incident light, and having good open-circuit voltage (Voc) and fill factor (FF), among others. It is still another object of the present invention to provide a  
25 method for producing the same.

[Means for Solving the Problem]

[0015]

The present invention has been accomplished by the extensive studies to solve the above problems, and has the following constitutions.

[0016]

5       The first aspect of the present invention is a stacked photovoltaic element comprising a plurality of unit photovoltaic elements each composed of a pn- or pin-junction, connected to each other in series, wherein at least a zinc oxide layer is provided at  
10   least one position between the unit photovoltaic elements, and the zinc oxide layer has resistivity varying in the thickness direction.

      In the first aspect, zinc oxide on a side of being in contact with a p-layer of the pn- or pin-junction  
15   has a higher resistivity than that on a side of being in contact with an n-layer of the pn- or pin-junction in the zinc oxide layer.

      In the first aspect, the resistivity of zinc oxide continuously decreases from the p-layer side towards  
20   the n-layer side.

      In the first aspect, the resistivity of zinc oxide is preferably  $2 \times 10^0 \Omega\text{cm}$  or more and  $5 \times 10^3 \Omega\text{cm}$  or less.

      In the first aspect, the highest resistant portion of zinc oxide preferably has  $5 \times 10^2 \Omega\text{cm}$  or more and  
25    $5 \times 10^3 \Omega\text{cm}$  or less.

      Of the plurality of the unit photovoltaic elements for the first aspect, at least one unit photovoltaic

element has a pin-junction comprising an i-type layer suitably composed of an amorphous Si:H.

Of the plurality of the unit photovoltaic elements for the first aspect, at least one unit photovoltaic  
5 element has a pin-junction comprising an i-type layer suitably composed of microcrystalline Si.

Of the plurality of the unit photovoltaic elements for the first aspect, at least one unit photovoltaic element has a pin-junction comprising an i-type layer  
10 suitably composed of single-crystalline or polycrystalline Si.

[0017]

The second aspect of the present invention is a method for producing a stacked photovoltaic element  
15 comprising an intermediate layer between unit photovoltaic elements each having a pn- or pin-junction, wherein a first layer mainly composed of indium oxide is stacked on at least one interface with the photovoltaic element and then a second layer mainly  
20 composed of zinc oxide is stacked on the first layer to form the intermediate layer.

In the method of the second aspect, the second layer is formed to be thicker than the first layer.

In the method of the second aspect, the first  
25 layer is formed to have a thickness of 1 nm or more and 50 nm or less.

In the method of the second aspect, the second

layer is formed at a rate higher than that of the first layer.

In the method of the second aspect, the second layer is formed at a temperature lower than that of the first layer.

[0018]

The third aspect of the present invention is a stacked photovoltaic element comprising an intermediate layer between unit photovoltaic elements each having a pn- or pin-junction, wherein the intermediate layer comprises a first layer and a second layer stacked in this order on at least one interface with a photovoltaic element, the first layer being mainly composed of indium oxide and the second layer being mainly composed of zinc oxide.

In the third aspect, the second layer is thicker than the first layer.

In the third aspect, the first layer has a thickness of 1 nm or more and 50 nm or less.

In the third aspect, the second layer has a transmittance higher than that of the first layer at a wavelength of 800 nm.

[Effect of the Invention]

[0019]

The first aspect of the present invention can provide a stacked photovoltaic element exhibiting a high conversion efficiency realized by efficiently

absorbing light over an entire wavelength range of incident light, reducing short-circuit current flowing an electrical defect and improving juncture between the zinc oxide layer and semiconductor layer.

5 [0020]

The second aspect and third aspect brings excellent effects, the former providing a method for producing a stacked photovoltaic element and the latter providing a stacked photovoltaic element, where the  
10 stacked photovoltaic element is of high conversion efficiency, can efficiently collect energy over an entire wavelength range of incident light, and has good open-circuit voltage (Voc) and fill factor (FF).

[Detailed Description of the Preferred Embodiments]

15 [0021]

The preferred embodiments of the present invention are described by referring to the attached drawings. It should be understood that the present invention is not limited to these embodiments.

20 [0022]

A solar cell comprising two photovoltaic elements will be described as an example of the stacked photovoltaic element of the present invention. However, the present invention is not limited to this  
25 structure, and can be applied to a stacked photovoltaic element comprising three or more photovoltaic elements.

[0023]

Fig. 3 outlines a cross-sectional structure of the two-layers-stacked photovoltaic element 300 as one embodiment of the present invention. It has on a substrate 301 of a metal or the like which has a reflection layer stacked thereon, the second photovoltaic element 302, second zinc oxide layer 303, first zinc oxide layer 304, first photovoltaic element 305 and transparent electrode 306 stacked in this order. A semiconductor which constitutes the photoactive section for the first photovoltaic element 305 has a larger band gap than that of a semiconductor which constitutes the photoactive section for the second photovoltaic element 302. This means that the stacked photovoltaic element 300 is designed in such a way that the first photovoltaic element 305 absorbs light in a short wavelength range while the second photovoltaic element 302 absorbs light in a long wavelength range. The first zinc oxide layer 304 and first photovoltaic element 305 have a different refractive index. Therefore, multiple reflection can be created by adjusting the thickness of each layer to efficiently enhance reflectivity in the short wavelength range, and thereby to increase the quantity of light absorbed by the first photovoltaic element 305. The second zinc oxide layer 303 is designed to have a higher resistivity than that of the first zinc oxide layer 304.

[0024]

Fig. 4 schematically illustrates power-generating operation of the first stacked photovoltaic element of the present invention. An electrical defect in the first photovoltaic element acts as a short-circuit current passage. When the electrical defect 402 in the first photovoltaic element 305 is close to the electrical defect 403 in the second photovoltaic element 302, no deterioration of the photovoltaic element characteristics is caused by these defects, because the transparent electrode 306 is removed by the shunt passivation treatment carried out after the stacked photovoltaic element is assembled. When these defects are apart from each other at a distance, on the other hand, the characteristics may be deteriorated, because of insufficient shunt passivation treatment. Although the first photovoltaic element 305 is provided with the first zinc oxide layer 304 of lower resistivity on the substrate side surface, it is sufficiently thin and causes spread of short-circuit current in the lateral direction to only a limited extent. Therefore, it little deteriorates the characteristics.

[0025]

On the other hand, in the vicinity of the electrical defect in the second photovoltaic element 302, the electroconductive zinc oxide layer is present,

and the defect acts as a short circuit in the photovoltaic element while power is being generated. However, the second photovoltaic element 302 has the second zinc oxide layer 303 of higher resistivity on the surface of the element 302 (upper layer surface),  
5       whereby short-circuit current spreads via the first zinc oxide layer 304 of lower resistivity while its spread in the lateral direction is limited. A total thickness of the first zinc oxide layer 304 and second  
10       zinc oxide layer 303 is limited to a level suitable for the selective reflection layer, and spread of the short-circuit current can be efficiently prevented by combination of the higher and lower resistivities.  
[0026]

15       The electrical polarities at each junction of the stacked structure consisting of the second photovoltaic element, second and first zinc oxide layer and first photovoltaic element provided in this order are, for example, as shown in Fig. 2, a combination of n-  
20       /n+/n++, i.e., the second zinc oxide layer 202 of the lowest carrier concentration (n-), the first zinc oxide layer 203 of higher carrier concentration (n+) and the n-type semiconductor layer 204 of the first photovoltaic element of the highest carrier  
25       concentration (n++) are stacked in this order. In Fig. 2, 201 denotes a substrate, 202: second zinc oxide layer of n- type, 203: first zinc oxide layer of n+



type, 204: first photovoltaic element as the n- type  
semiconductor layer of n++ type, 205: transparent  
electrode, 206: second photovoltaic element, 207:  
stacked zinc oxide layer, and 208: first photovoltaic  
5 element.

[0027]

The n-type zinc oxide layer can have a controlled  
bulk carrier concentration by the production  
conditions. It is considered that light-generating  
10 carrier can be collected more efficiently by increasing  
carrier concentration in the n-type zinc oxide layer  
stepwise or continuously from the p-type semiconductor  
layer side of the second photovoltaic element towards  
the n-type semiconductor layer side of the first  
15 photovoltaic element, because increasing or decreasing  
trend of concentration of the carrier of the same  
polarity is set in one direction including the n-type  
semiconductor layer of the first photovoltaic element,  
thereby efficiently connecting these elements to each  
20 other at the band junction, although the concept is not  
fully substantiated.

[0028]

The zinc oxide layer as the intermediate layer has  
a higher resistivity, preferably  $2 \times 10^0 \Omega\text{cm}$  or more and  
25  $5 \times 10^3 \Omega\text{cm}$  or less for both the first and second zinc  
oxide layers, than recent zinc oxide layers of which  
the resistivity has been greatly decreased. The

intermediate layer having a resistivity in the above range has a lower carrier concentration than that of the n-type semiconductor layer of the first photovoltaic element, conceivably resulting in improved  
5 junction. On the other hand, short-circuit current is considered to diffuse in the zinc oxide layer, unless zinc oxide has a resistivity of  $5 \times 10^2 \Omega\text{cm}$  or more and  $5 \times 10^3 \Omega\text{cm}$  or less in the high-resistivity portion, to deteriorate the characteristics.

10 [0029]

The zinc oxide layer preferably transmits at least 50% of light having a wavelength of 800 nm. The wavelength range of solar light which can be effectively utilized by the photovoltaic element is  
15 approximately from 300 to 1200 nm in consideration of its spectral pattern. The cell on the zinc oxide layer absorbs light of short wavelength, and hence it is preferable for the zinc oxide layer to effectively transmit light of long wavelength. Therefore, it  
20 preferably transmits at least 50% of light having a wavelength of 800 nm, which represents the long wavelength.

[0030]

The stacked photovoltaic elements of the second  
25 and third aspects of the present invention will be now described.

[0031]

First, the intermediate layer as the feature of these aspects is described. In each of these aspects, a stacked photovoltaic element is formed by stacking a plurality of unit photovoltaic elements each containing  
5 a pn- or pin-junction, wherein a first layer mainly composed of indium oxide is stacked on at least one interface with a photovoltaic element and then a second layer mainly composed of zinc oxide is stacked on the first layer to form the intermediate layer. The  
10 stacked photovoltaic element of the above structure brings the following effects. The structure and each component of the stacked photovoltaic element of each aspect will be described in detail later.  
[0032]

15 Incorporation of the intermediate layer of the above structure can prevent deterioration of the Voc and FF values, and allows the stacked photovoltaic element to exhibit the excellent characteristics for extended periods of use. The Voc and FF values tend to  
20 deteriorate, when an intermediate layer of zinc oxide alone is provided on the interface with the photovoltaic element, while depending on conditions under which zinc oxide is produced, its resistivity and thickness, among others. This phenomenon is not  
25 notably observed when a photovoltaic element is provided on zinc oxide. For example, zinc oxide may be used for a reflection layer to be provided on a

substrate type photovoltaic element. In such a case, deterioration of the Voc or FF characteristics is not observed notably, from which it is considered that the deteriorated characteristics result from the process  
5 itself for forming the zinc oxide layer on the interface with the photovoltaic element. In other words, it is conceivably related to the process in which the semiconductor is formed on zinc oxide in a reducing atmosphere whereas zinc oxide is formed on the  
10 interface with the photovoltaic element in an oxidative atmosphere: oxygen in zinc oxide formed on the interface with the photovoltaic element is depleted by the atom on the interface with the photovoltaic element to oxidize the semiconductor, resulting in formation of  
15 a modified layer in the interface between the photovoltaic element and zinc oxide.

[0033]

The above tendency is more noted when the zinc oxide layer is formed in the presence of oxygen or  
20 moisture. Its characteristics are further deteriorated when the film formed by sputtering or the like, which generates the oxygen ion, because of the ion-caused damages to the interface with the photovoltaic element. The phenomenon is still more noted when the zinc oxide  
25 layer is formed on a p-type layer, which is more sensitive to the Voc characteristics.

[0034]

When an intermediate layer composed mainly of indium oxide is provided on the interface with the photovoltaic element, on the other hand, shunt resistance tends to decrease to deteriorate the Voc and  
5 FF values depending on conditions under which zinc oxide is produced, content of a dopant, e.g., tin, its resistivity and thickness, among others. The decreased shunt resistance conceivably results from generation of leakage current flowing in the intermediate layer in  
10 the lateral direction, because indium oxide generally has a lower resistivity than that of zinc oxide. Moreover, indium oxide is more sensitive to a reducing atmosphere than zinc oxide, and indium separates out when a photovoltaic element is formed on indium oxide,  
15 thereby deteriorating the characteristics, including long-term reliability.

[0035]

No deterioration of the characteristics, in particular Voc and FF, is observed, when a thin, first  
20 layer mainly composed of indium oxide and then second layer mainly composed of zinc oxide are stacked on the interface with the photovoltaic element to form the intermediate layer. This conceivably results from the improved interface between the first layer and  
25 photovoltaic element, although not fully substantiated. It is expected that flowing of leakage current in the lateral direction can be made difficult when the first

layer has an adequate resistivity and thickness, and photocurrent can be increased when the second layer is adequately thick.

[0036]

5           The first layer preferably has a sufficient resistivity so as to make difficult the flowing of leakage current in the lateral direction and is adequately thin. The photovoltaic element is attached frequently at high temperature, and indium can diffuse  
10 when exposed to high temperature continuously for extended periods to deteriorate the characteristics including long-term reliability. It is preferable, also viewed from the above, the first layer is adequately thin. Therefore, the first layer mainly  
15 composed of indium oxide preferably has a thickness of 1 nm or more and 50 nm or less, more preferably 3 nm or more and 40 nm or less, still more preferably 5 nm or more and 30 nm or less.

[0037]

20           The intermediate layer, on the other hand, reflects more light to the photovoltaic element provided thereon as its thickness increases. Therefore, the second layer is preferably thicker than the first layer.

25 [0038]

          The first layer preferably has a lower resistivity than the second layer. Each layer preferably has an

average transmittance of 80% or more for the visible light, in particular the transmittance of 80% or more at a wavelength of 800 nm (light of long wavelength side). Moreover, the second layer preferably has a  
5 higher transmittance at a wavelength of 800 nm than the first layer.

[0039]

As discussed above, the second and third aspects of the present invention are characterized by the  
10 optimum design in which at least two oxide films of different characteristics are functionally separated from each other in accordance with the characteristics of each film.

[0040]

15 The intermediate layer has a certain thickness. The increase of a deposition rate is economically advantageous because of decreased tact time, but is liable to deteriorate the characteristics. Formation of the first layer at a lower rate can secure the good  
20 interfacial characteristics while minimizing the damages. No deterioration of the characteristics is observed, when the first layer is formed at a lower rate and then the second layer at a higher rate. Therefore, the second layer is preferably formed at a  
25 higher rate than the first layer.

[0041]

Moreover, indium tends to diffuse, and hence the

intermediate layer is preferably formed at as low temperature as possible after the first layer is formed. It should be noted, however, that decreasing deposition temperature tends to deteriorate the transmittance of indium oxide. Therefore, a certain temperature level is essential for forming the indium oxide layer. The zinc oxide layer, on the other hand, tends to have a higher transmittance to have the enhanced Jsc value, when formed at lower temperature. Increasing deposition temperature, however, generates more stress in the zinc oxide layer, tending to cause separation of the stacked structure at the intermediate layer. Therefore, the second layer is preferably formed at a lower temperature than the first layer. The first layer is preferably formed at 150°C or higher but 300°C or lower, and the second layer at 50°C or higher but 250°C or lower. Moreover, the second layer is more preferably formed at a temperature lower by at least 40°C.

[0042]

Next, the construction of the stacked photovoltaic element of the second and third aspect of the present invention will be described.

[0043]

Fig. 8 schematically outlines a cross-sectional structure of one embodiment of the stacked photovoltaic element of the second and third aspect of the present



invention. The stacked photovoltaic element 800 has on the electroconductive substrate 801 of a metal or the like, the light reflection layer 802, second photovoltaic element 803, the intermediate layer 806  
5 (consisting of the first layer 804 mainly composed of indium oxide and the second layer 805 mainly composed of zinc oxide), first photovoltaic element 807 and transparent electrode 808 stacked in this order as shown in Fig. 8. It is designed in such a way that a  
10 semiconductor which constitutes the photoactive section for the first photovoltaic element 807 has a larger band gap than a semiconductor which constitutes the photoactive section for the second photovoltaic element 803, or the photoactive section of the former is made  
15 thinner than the latter, thereby allowing the first photovoltaic element 807 to absorb light in a short wavelength range while allowing the second photovoltaic element 803 to absorb light in a long wavelength range. The intermediate layer 806 functions to reflect a part  
20 of light and thereby to increase quantity of light absorbed by the first photovoltaic element 807. The intermediate layer 806 may be provided with irregularities on the surface.

[0044]

25 Fig. 7 schematically outlines the method of the present invention for producing the stacked photovoltaic element of the present invention as shown

in Fig. 8.

[0045]

On the substrate 700 having a reflection layer 701 and second photovoltaic element 702 formed thereon as shown in Fig. (a) of 7, a layer 703 mainly composed of indium oxide is deposited as shown in (b) of Fig. 7. The layer 704 mainly composed of zinc oxide is deposited as shown in (c) of Fig. 7. The first photovoltaic element 706 is further deposited thereon as shown in (d) of Fig. 7. Then, the transparent electrode is deposited thereon. The deposition of each layer in this order complete the stacked photovoltaic element with the intermediate layer 705 (consisting of the layer 703 mainly composed of indium oxide and layer 704 mainly composed of zinc oxide) between the photovoltaic elements.

[0046]

Fig. 9 schematically outlines a cross-sectional structure of another embodiment of the stacked photovoltaic element of the present invention. The stacked photovoltaic element 900 has on the transparent, insulating substrate 901 of glass or the like, transparent electrode 908, first photovoltaic element 907, intermediate layer 906 (consisting of the first layer 904 mainly composed of indium oxide and second layer 905 mainly composed of zinc oxide), second photovoltaic element 903 and electroconductive, light

reflection layer 902 stacked in this order. In this case, incident light enters the stacked photovoltaic element 900 from the transparent, insulating substrate 901 side. The intermediate layer 906 may be provided  
5 with irregularities on the surface.

[0047]

Next, each component for the stacked photovoltaic element of the present invention is described.

[0048]

10 [Substrate]

The material for the substrate which constitutes the stacked photovoltaic element of the present invention is not limited. It may be an electroconductive or insulating material of any type.  
15 The electroconductive materials include metals, e.g., plated steel, NiCr, stainless steel, Al, Cr, Mo, Au, Nb, Ta, V, Ti, Pt, Pb, Sn and an alloy thereof. The insulating materials include synthetic resins, e.g., polyester, polyethylene, polycarbonate, cellulose  
20 acetate, polypropylene, polyvinyl chloride, polyvinylidene chloride, polystyrene and polyamide; and glass, ceramics and paper. The particularly preferable materials are stainless steel as the metal substrate, and glass, ceramics and polyimide as the insulating  
25 substrate. A transparent, insulating substrate is used for the stacked photovoltaic element with incident light entering from the substrate side, and glass is

suitable for the substrate.

[0049]

The substrate surface may be smooth or of irregular texture with irregularities having the maximum height of 0.1 to 1.0  $\mu\text{m}$ . A stainless steel substrate may have a surface of irregular texture by etching with an acidic solution.

[0050]

Thickness of the substrate may be adequately set to give a desired stacked photovoltaic element by stacking the layers one on another as intended. When the stacked photovoltaic element is required to be flexible, it may be as thin as possible so long as it can sufficiently work as a support. However, it normally has a thickness of 10  $\mu\text{m}$  or more in consideration of production, handling and mechanical strength.

[0051]

[Reflection Layer]

The reflection layer for the stacked photovoltaic element of the present invention is made of a deposited film of a metal which has a high reflectivity of light from the visible to near-infrared ray, e.g., Ag, Al, Cu and an alloy thereof. It is suitably formed by, e.g., vacuum evaporation, sputtering or electrolytic deposition from an aqueous solution. It is preferably 10 to 5000 nm thick. It is preferably provided with

irregularities on the surface for irregular reflection. It is also preferably provided with an increased reflectance layer to increase quantity of reflected light.

5 [0052]

The materials for the increased reflectance layer include ZnO, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, ITO, TiO<sub>2</sub>, CdO, Cd<sub>2</sub>SnO<sub>4</sub>, Bi<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub> and Na<sub>x</sub>WO<sub>3</sub>. The increased reflectance layer is suitably formed by vacuum evaporation, sputtering, 10 electrolytic deposition, CVD, spraying, spin-on, dipping or the like of the above material. Its thickness is preferably 50 nm to 10 μm, although the optimum thickness varies depending on inherent reflectivity of the material used. The increased 15 reflectance layer is preferably provided with irregularities on the surface for increasing light scattering. For example, in the sputtering method sputtering conditions may be selected to provide irregularities based on the grain boundaries.

20 [0053]

[Photovoltaic Layer (Photovoltaic Element)]

The semiconductors useful for the stacked photovoltaic element of the present invention include single-crystalline, poly-crystalline, microcrystalline 25 and amorphous materials of IV, III-V, II-VI, I-III-VI<sub>2</sub> groups. The IV group materials include C, Si and Ge and an alloy thereof, III-V group materials AlAs, AlSb,

GaN, GaP, GaAs, GaSb, InP and InAs, II-VI group materials ZnSe, ZnS, ZnTe, CdS, CdSe, CdTe and Cu<sub>2</sub>S, and I-III-VI<sub>2</sub> group materials CuInSe<sub>2</sub>. Of these, silicon-based semiconductors are more preferable. The  
5 single-crystalline, poly-crystalline, microcrystalline and amorphous semiconductors are suitably used.

[0054]

The photovoltaic layer for the stacked photovoltaic element of the present invention contains  
10 a pn- or pin-junction.

[0055]

The stacked photovoltaic element of the present invention comprises at least two photovoltaic layers. The semiconductors for these photovoltaic layers may be  
15 the same or different material. However, in the preferable structure, a photovoltaic layer using a semiconductor which can more efficiently absorb light of shorter wavelengths and another photovoltaic layer using a semiconductor which can more efficiently absorb  
20 light of longer wavelengths are stacked in this order from the incident light side, because light of shorter wavelength is more easily absorbed.

[0056]

[Zinc Oxide Layer]

25 The stacked photovoltaic element of the first aspect of the present invention has an intermediate layer composed of zinc oxide in at least one position

between the photovoltaic layers (unit photovoltaic elements).

[0057]

The zinc oxide layer for the present invention can  
5 be suitably formed by vacuum evaporation, DC magnetron  
sputtering, RF magnetron sputtering, electrolytic  
deposition, electroless plating, CVD, MOCVD, spraying,  
spin-on, dipping, sol-gel process or the like. The  
generally known dopants for adjusting its resistivity  
10 include Al, B, Ga and In. The other known dopants  
include tetravalent metals, e.g., Si, Ge, Ti and Zr.  
When a common vacuum evaporation or sputtering method  
is employed, zinc oxide (target or the like) may be  
sintered after previously adding the dopant at a  
15 desired content to zinc oxide.

[0058]

The zinc oxide layer has a varying reflectivity to  
reflect more light having a wavelength shorter than the  
wavelength  $\lambda_m$ , at which the second photovoltaic element  
20 attains the highest spectral characteristics, and to  
reflect less light having a wavelength longer than the  
wavelength  $\lambda_m$ , in order to efficiently convert energy  
of incident light over an entire wavelength range. The  
zinc oxide layer preferably has a transmittance of 80%  
25 or more, to efficiently utilize incident light.

[0059]

The zinc oxide layer for the present invention has

a resistivity varying in the thickness direction to prevent deteriorated element characteristics caused by shunt, as the problem involved in the conventional layer, while keeping its function as a selective  
5 reflection film. Its resistivity is preferably  $2 \times 10^0$   $\Omega\text{cm}$  or more and  $5 \times 10^3$   $\Omega\text{cm}$  or less. The high resistivity portion of the zinc oxide layer is preferably  $5 \times 10^2$   $\Omega\text{cm}$  or more and  $5 \times 10^3$   $\Omega\text{cm}$  or less. Its thickness is preferably 0.2 to  $2\mu\text{m}$  in consideration  
10 of its reflectivity, series resistance and irregularities on the surface.

[0060]

[Intermediate Layer]

The intermediate layer for the stacked  
15 photovoltaic element of the second and third aspects of the present invention comprises two layers, one being mainly composed of indium oxide and the other mainly composed of zinc oxide. The layer mainly composed of indium oxide may contain a trace quantity of another  
20 component, e.g., Mg, Zn, Sn or Sb.

[0061]

The layer mainly composed of zinc oxide may contain a trace quantity of another component, e.g., Al, Sn, In, Fe, Ga, Co, Si, Ti, Ge or Sb.

25 [0062]

The intermediate layer may contain a still another component, e.g.,  $\text{SnO}_2$ ,  $\text{TiO}_2$ ,  $\text{CdO}$ ,  $\text{Cd}_2\text{SnO}_4$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{MoO}_3$  or



$\text{Na}_x\text{WO}_3$ .

[0063]

The intermediate layer may be suitably formed by vacuum evaporation, sputtering, electrolytic  
5 deposition, CVD, spraying, spin-on, dipping or the like.

[0064]

The intermediate layer formed may be further treated by wet etching, dry etching or the like to have  
10 irregularities on the surface. It is formed by stacking the layer mainly composed of indium oxide on the interface with the semiconductor and then the layer mainly composed of zinc oxide.

[0065]

15 [Transparent Electrode]

The materials for the transparent electrode for the stacked photovoltaic element of the present invention include indium oxide, tin oxide, indium-tin oxide or zinc oxide. The transparent electrode is  
20 formed by sputtering, vacuum evaporation, chemical vapor deposition, ion plating, ion beam or ion beam sputtering. It may be also formed by electrolytic deposition or immersion in an aqueous solution of a metallic ion, e.g., that containing nitric, acetic or  
25 ammonia group. It preferably has a sufficient thickness to satisfy the requirements as an antireflection film.

[Examples]

[0066]

The examples as the preferred embodiments of the present invention are described in detail by referring to the attached drawings. These embodiments describe  
5 example for a solar cell as a stacked photovoltaic element comprising two photovoltaic layers (unit photovoltaic elements), produced by stacking on a substrate, a reflection layer, a photovoltaic element  
10 of microcrystalline silicon, an intermediate layer and a photovoltaic element of amorphous silicon in this order from the substrate side. However, the present invention is by no means limited to the above structure, and the number of the photovoltaic elements  
15 may be increased as required.

[0067]

[Example 1]

In Example 1, the stacked photovoltaic element of the first aspect of the present invention having the  
20 pin-type second photovoltaic element 302 with the i-layer of intrinsic microcrystalline Si, pin-type first photovoltaic element 305 with the i-layer of intrinsic amorphous Si:H and the intermediate layer of zinc oxide (refer to Fig. 3) was produced.

25 [0068]

The substrate 301, 45 mm square and 0.15 mm thick, was of flat stainless steel (SUS 430), commonly

referred to as BA-finished one. It was put in a commercial DC magnetron sputtering unit (not shown), which was evacuated to a pressure of  $10^{-3}$  Pa or less. [0069]

5 Argon was blown into the unit at  $30 \text{ cm}^3/\text{min}$  (normal conditions) to keep pressure inside at  $2 \times 10^{-1}$  Pa. A DC power of 120 W was applied to an aluminum target (diameter: 6 inches) for 90 seconds to form a thin film of aluminum with a thickness of 70 nm on the  
10 substrate, while the substrate was kept unheated. Then, a DC power of 500 W was applied to a zinc oxide target (diameter: 6 inches), after the electrical connection was changed, for 30 minutes to form the reflection layer of zinc oxide with a thickness of  
15 about 500 nm, while the substrate was heated at  $200^\circ\text{C}$ . [0070]

Fig. 5 schematically illustrates one embodiment of suitable apparatus for producing a semiconductor layer for the stacked photovoltaic element of the present  
20 invention, where the deposited film forming apparatus 500 comprises the following major components; 501: load chamber, 502: RF chamber for the n-type layer, 503: chamber for the i-type layer of microcrystalline silicon, 504: RF chamber for the i-type layer of  
25 amorphous silicon, 505: RF chamber for the p-type layer and 506: unload chamber. These chambers are isolated from each other by a gate valve 507, 508, 509, 510 or

511 so that feed gases of the respective chambers are not mixed with each other.

[0071]

The chamber 503 for the i-type layer of  
5 microcrystalline silicon is composed of the heater 512 for heating the substrate and plasma CVD chamber 513. The RF chamber 502 is composed of the heater 514 for depositing the n-type layer and deposition chamber 515 for depositing the n-type layer, the RF chamber 504 the  
10 heater 516 for depositing the i-type layer and deposition chamber 517 for depositing the i-type layer, and the RF chamber 505 the heater 518 for depositing the p-type layer and deposition chamber 519 for depositing the p-type layer. The substrate is  
15 supported by the substrate holder 521 to run on the rail 520 by a roller driven from an outside power source. In the plasma CVD chamber 513, a microcrystal is deposited by microwave plasma CVD or VHF plasma CVD.

[0072]

20 The deposited film forming apparatus of the above structure was used to form, as the second photovoltaic element 302, pin-type photovoltaic element whose i-type layer was of intrinsic microcrystalline Si under the deposition conditions given in Table 1 by the following  
25 procedure.

[0073]

First, the substrate 301 provided with a

reflection layer was set on the substrate holder 521 and then on the rail 520 in the load chamber 501. The load chamber 501 was then evacuated to a vacuum of several hundreds mPa or less.

5 [0074]

Next, the gate valve 507 was opened, and the substrate holder 521 was moved into the deposition chamber 515 for depositing the n-type layer in the chamber 502, where the n-type layer was deposited to a given thickness using a given feed gas, while the gate valves 507, 508, 509, 510 and 511 were kept closed. The chamber was sufficiently evacuated, and the gate valve 508 was opened to move the substrate holder 521 into the deposition chamber 503. Then the gate valve  
10 508 was closed.  
15

[0075]

The substrate was heated to a given temperature by the heater 512, a necessary quantity of the feed gas was charged in the chamber, and given microwave or VHF energy was introduced into the deposition chamber 513 which was evacuated to a given vacuum level, to generate a plasma therein to deposit the i-type layer of microcrystalline silicon to a given thickness. The chamber 503 was sufficiently evacuated, and the gate valves 509 and 510 were opened to move the substrate holder 521 from the chamber 503 to the chamber 505.  
20  
25

[0076]

After the substrate holder 521 was moved into the deposition chamber 519 for depositing the p-type layer in the chamber 505, the substrate was heated to a given temperature by the heater 518. A necessary quantity of  
5 the feed gas to deposit the p-type layer was charged into the deposition chamber 519 into which RF energy was introduced to deposit the p-type layer to a given thickness, while the chamber was kept at a given vacuum level.

10 [0077]

Similarly as in the above, the deposition chamber 519 was sufficiently evacuated, and the gate valve 511 was opened to move the substrate holder 521 into the unload chamber 506. Then, all gate valves were closed  
15 and nitrogen gas was charged into the unload chamber 506, and the substrate was cooled with nitrogen gas in the unload chamber 506, while all of the gate valves were closed. Then, the substrate holder 521 was taken out of the unload chamber 506, after the discharge  
20 valve was opened.

[0078]

[ Table 1]

		Gas for layer formation (cm <sup>3</sup> /minute under normal conditions)				Power density (W/cm <sup>2</sup> )		Pressure (Pa)	Substrate temperature (°C)	Thickness of layer (nm)
		SiH <sub>4</sub>	H <sub>2</sub>	PH <sub>3</sub> (diluted to 2% with H <sub>2</sub> )	BF <sub>3</sub> (diluted to 2% with H <sub>2</sub> )	RF	VHF			
Second photovoltaic element	N2	2	48	0.5		0.04		180	225	20
	I2	25	750				0.2	40	250	2000
	P2	0.025	35		1	1.2		270	165	5

[0079]

Next, the substrate, on which the layers up to the second photovoltaic element 302 was formed, was removed from the substrate holder 521, and set on the substrate holder 601 in the DC magnetron sputtering apparatus 600 for forming a zinc oxide layer, shown in Fig. 6. Then, the apparatus was evacuated to a pressure of  $10^{-3}$  Pa or less.

[0080]

10       The substrate holder 601 was electrically insulated, and could keep the photovoltaic element as the sample floated. The apparatus was kept at a pressure of  $2 \times 10^{-2}$  Pa while argon gas was supplied at 50 sccm, and oxygen gas and vaporized  $H_2O$  gas were  
15       supplied at a rate given in Table 2 within 0.1 to 5 sccm, all via the gas inlet tube 602. The substrate holder 601 was heated by the heater 603 to keep the substrate at  $150^\circ\text{C}$ . A DC power of 500 W was applied from the DC power source 605 onto the Al-doped zinc  
20       oxide (ZnO) target 604 (diameter: 6 inches) for 10 minutes, to deposit the second zinc oxide layer 303 with a thickness of about  $0.5 \mu\text{m}$  on the substrate. The target 604 was surrounded by the earth shield 606, to prevent diffusion of the plasma and to stabilize the  
25       discharge. At the same time, a quartz substrate (45 by 45 mm) was set on the substrate holder to deposit thereon the same layer of zinc oxide for the analysis



of its electrical properties.

[0081]

On each of the zinc oxide layers 303, Samples A to J given in Table 2 formed on each substrate, the first  
5 zinc oxide layer 304 was deposited under the conditions of A to J as given in Table 2. A total of 100 samples were prepared. At the same time, a quartz substrate (45 by 45 mm) was set on the substrate holder to  
10 deposit thereon the same layer of zinc oxide for the analysis of its electrical properties.

[0082]

[Table 2]

Sample No.	Oxygen flow rate (sccm)	H <sub>2</sub> O flow rate (sccm)
A	0.1	10
B	0.3	10
C	0.4	10
D	0.5	10
E	0.8	10
F	1.0	10
G	2.0	5
H	5.0	5
1	10.0	2
J	15.0	2

[0083]

Next, the deposited film forming apparatus 500 was  
15 again used to form, on a substrate on which the above

intermediate layer (zinc oxide layer) was formed, as  
the first photovoltaic element 305, pin-type  
photovoltaic element whose i-type layer was of  
intrinsic amorphous Si:H under the deposition  
5 conditions given in Table 3 by the following procedure.  
[0084]

First, the n-type layer was deposited under given  
conditions to a given thickness in a manner similar to  
that described above. The gate valves 508 and 509 were  
10 opened and the substrate holder 521 was moved into the  
deposition chamber 504, after it was sufficiently  
evacuated. Then, these valves were closed.  
[0085]

The substrate was heated to a given temperature by  
15 the heater 516, and a necessary quantity of the feed  
gas was charged in the chamber. Given RF energy was  
introduced into the deposition chamber 517, which was  
evacuated to a given vacuum level, to generate a plasma  
therein to deposit the i-type layer of amorphous Si:H  
20 to a given thickness by adjusting deposition time. The  
chamber 504 was sufficiently evacuated, and the gate  
valve 510 was opened to move the substrate holder 521  
from the chamber 504 to the chamber 505.  
[0086]

25 The p-type layer was deposited to a given  
thickness in a manner similar to that described above.  
[0087]